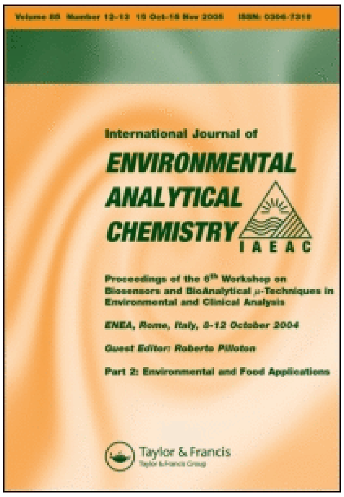

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Isotopic Characterization of Lead in the Scottish Upland Environment

J. R. Bacon[a]; M. L. Berrow[a]; C. A. Shand[a]
[a] The Macaulay Land Use Research Institute, Aberdeen, U.K.

To cite this Article Bacon, J. R. , Berrow, M. L. and Shand, C. A.(1995) 'Isotopic Characterization of Lead in the Scottish Upland Environment', International Journal of Environmental Analytical Chemistry, 59: 2, 253 — 264
To link to this Article: DOI: 10.1080/03067319508041332
URL: http://dx.doi.org/10.1080/03067319508041332

Intern. J. Environ. Anal. Chem., Vol. 59, pp. 253–264
Reprints available directly from the publisher
Photocopying permitted by license only

ISOTOPIC CHARACTERIZATION OF LEAD IN THE SCOTTISH UPLAND ENVIRONMENT

J. R. BACON, (the late) M. L. BERROW and C. A. SHAND

The Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen AB9 2QJ, U.K.

(Received, 22 November 1993; in final form, 15 January 1994)

Experimental plots have been set up at two Research Stations in upland areas of Scotland with the intention of characterising environmental samples using lead isotopic composition which varies according to the original source of the lead. Thermal ionisation mass spectrometry (TIMS) was used to measure lead isotope ratios with high precision. The $^{206}Pb/^{207}Pb$ ratios in rainwater were in the range from 1.101 to 1.153 over a period of two years at the two sites. Low ratios were associated with the very low ratios found in Britain in petrol additives during that period whereas higher ratios indicated a larger component derived from industrial sources at the Hartwood site. The $^{206}Pb/^{207}Pb$ ratios in the surface (0–2.5 cm) soil from a roadside plot were low (1.1126 and 1.1159 in 1989 and 1990, respectively) but the ratios in surface soils in plots distant from the road were considerably higher. Whereas the lead in roadside soil had a $^{206}Pb/^{207}Pb$ ratio indicating its source to be predominantly in recent petrol lead, there were significant components from other sources in the soils away from the road. The washing of grass samples resulted in no significant change in the lead isotope ratios. The lead isotope ratios measured in grass samples reflect the isotopic character of current atmospheric inputs but those in surface soil samples are an integrated record of atmospheric deposition over a long period of time. An undisturbed plot under a tree canopy had high concentrations of lead in the surface soil and low $^{206}Pb/^{207}Pb$ ratios. The ratios in fallen leaves on this plot were slightly but significantly lower than those in the grass grown on the plot. It would appear that the tree canopy is effective at scavenging lead carried in the atmosphere.

KEY WORDS: Lead, stable isotope composition, aerial deposition, soil pollution, rainwater lead, grass lead

INTRODUCTION

Trace amounts of lead occur naturally in rocks and soils but soil is also a major sink for anthropogenic lead. Contamination from industry, coal ash, paint, sewage sludge, mining and smelting, and petrol has resulted in widespread soil contamination such that anthropogenic inputs into the environment have been estimated to be 100 times the natural rate[1]. Urban areas in the U.K. have mean lead concentrations in surface soils in the range 100–400 $\mu g.g^{-1}$ whereas in rural areas the mean concentration is generally below 100 $\mu g.g^{-1}$ [2]. The latter are still considerably higher than those (5–40 $\mu g.g^{-1}$) found in deeper soil horizons which can be taken to represent natural lead levels in soils[3]. It would appear therefore that even rural soils have been contaminated by inputs of anthropogenic lead. Uncultivated surface soils from remote rural locations in Scotland, which generally have a high organic matter content, commonly have high lead concentrations (up to 500 $\mu g.g^{-1}$)[3] and it can be considered that lead pollution in surface soils is a widespread phenomenon. One approach for the study of these lead accumulations is the use of lead isotopic composition to identify the different sources of lead in a single sample.

Lead is the only industrially-important metal to have a naturally-variable isotopic composition. This arises from the slow (half life of 10^9–10^{10} years) radiogenic decay of uranium and thorium isotopes to form stable isotopes of lead. The relative amounts of lead isotopes formed are a function of the relative amounts of uranium and thorium and the period of time over which the decay has proceeded and this is reflected in the isotopic composition of any individual lead sample. Nier[4] first demonstrated this variability of isotopic composition in different lead ores and this fact has since been much exploited by isotope geologists to date rocks and provide information on the formation of rocks and ores. It was also recognised at an early stage that the isotopic composition could be exploited as an indicator of the source of lead pollution in the environmental. Chow and Johnson[5] demonstrated that lead in surface soil in an urban environmental was derived predominantly from alkyl lead products used in petrol. Rabinowitz and Wetherill[6] showed that it was possible to distinguish between different sources of lead contamination on the basis of stable isotopic composition. Lead could be traced from ore deposits and petrol to soils, vegetation and animals. A survey by Chow *et al.*[7] reported the isotopic composition of lead in ores, petrol, aerosols and soils from a number of locations world-wide.

Since these early studies there have been a considerable number of reports in which lead isotopic composition has been used to identify the source of lead in the environment. The studies have concentrated mainly on instances of pollution in urban and industrial environments in which the degree of contamination was high. Analysis of polluted soil profiles in both urban and rural locations in Australia indicated that the major source of the contamination was petrol lead.[8] Lead isotope abundances in river and estuarine sediments in South Wales[9], France[10] and Tokyo Bay[11] provided information on the history of contamination and the individual sources of contaminant lead. The two major sources of petrol lead and industrial emissions could be identified by their different isotopic signatures.

The prime route for introduction of anthropogenic lead into the environment is by atmospheric deposition and analysis of atmospheric aerosols can be used not only to identify the origin of the aerosols but also to trace movements of air masses. Air masses in the Mediterranean have been traced[12] and lead in the marine atmosphere of the North Sea correlated with general wind direction[13]. A comprehensive study of aerosol lead in Sweden[14] demonstrated that the isotopic nature of lead in the atmosphere can vary greatly over a short timescale (^{206}Pb/^{207}Pb changed from 1.133 to 1.105 to 1.156 in a 48-hour period) and thereby empasised the need to consider each situation separately both in time and location.

Most studies have addressed specific situations and there have been only a few attempts to characterize lead fully in the relatively unpolluted rural environment using isotopic composition. The studies of Fachetti and co-workers in Italy[15] and of Keinonen in Finland[16] were notable for the information they supplied on the isotopic nature of lead throughout the environment. Isotopic studies of lead in the Scottish environment have been limited. Sugden *et al.*[17] studied lead in the urban environment of Edinburgh and measured the isotopic composition of lead in petrol over the period 1989 to 1991. With one exception the ^{206}Pb/^{207}Pb ratio was in the range 1.056–1.093 which agreed closely with the figure (1.065 ± 0.003, n = 4) reported by Delves[18] for petrol lead in Edinburgh and Southampton. This would confirm that lead with a very low ^{206}Pb/^{207}Pb ratio was in widespread use at that time. Sugden *et al.*[19] have also measured lead isotope ratios in dated peat cores in remote locations in Scotland to give an indication of the isotopic nature of lead deposited in remote areas of Scotland over the last 200 years. The drop in ^{206}Pb/^{207}Pb ratio from 1.16 to 1.14 over the period 1940–1980 is in good agreement with the ratios measured[3] in surface soils in upland areas of Scotland (1.160–1.147).

The purpose of this study was to characterize the accumulations of heavy metals, in particular lead, in the environment in upland areas of Scotland using principally isotopic composition in the case of lead. The initial aim was to characterize lead isotopically in a number of environmental samples in order to understand the nature of the lead accumulations and to gain information on the origin and fate of lead in the Scottish environment. Previous studies have tended to be of contaminated environments such as roadside soils or urban air. The approach in this study was novel in that it addressed the situation of atmospheric inputs in relatively clean rural upland areas through a comprehensive characterization of field plots by analysis of soil, grass and rainwater over a long time period. The use of grass as a sensitive monitor of inputs of lead from the atmosphere is a new approach and is effective as an integrator of all possible inputs.

MATERIALS AND METHODS

Materials

Chemicals used in the preparation of samples for analysis were of the highest grade available. Acids (HNO_3, HCl, HF) were of commercial Aristar grade or redistilled in the laboratory. Deionised water was of 16MΩ quality.

Field plots

Fenced plots (1.5 m × 1.5 m) were set up in 1989 at three sites at the Glensaugh Research Station (N. E. Scotland about 30 miles S. W. of Aberdeen at an altitude of 300–400 m). One plot (Roadside, grid reference NO653804) was placed directly beside a road whereas the other two plots were distant (> 500 m) from the road, one (Hillside, grid reference NO658805) on an undisturbed area with indigenous vegetation and the other (Reseeded, grid reference NO659803) on an area fertilized and reseeded with a ryegrass/clover mix about 15 years ago. The plots were fenced so as to deny access both to grazing farm animals (sheep and cattle) and to burrowing animals such as rabbits.

In 1991 a further three plots were set up at the Hartwood Research Station (to the east of Motherwell, Central Scotland). This site was chosen to represent an area likely to be associated with atmospheric deposition of industrial origin such as the iron and steel works in the Motherwell area. One of the three plots (Bowhouse Bog, grid reference NS854586) was in a reseeded field directly beside a minor road, one (Moor, grid reference NS839597) was on uncultivated land in a large open field at the highest point of the farm facing in a westerly direction and the third (West Blaeberry Wood, grid reference NS844600) was on undisturbed soil in an area under tree cover and not used for farming activities. Both the Moor and the West Blaeberry Wood sites were distant (1100 and 700 m, respectively) from road traffic or farm buildings and were at an altitude of about 240 m above sea level.

Sample collection and preparation

Rainwater samples were collected on a regular monthly basis at monitoring stations distant from road traffic at the two Research stations. A volume of about 1 L was ideal but sometimes as little as 250 ml was only available and was usually sufficient. Samples were prepared for analysis by filtration (Whatman 542, 2.7 μm, 18.5 cm diameter) and gentle evaporation to dryness. The residue was taken up in 16 M HNO_3 (5 ml) and heated (80°C) on a hotplate to oxidize any organic matter and to bring the solution to dryness. This process was repeated with a further 5 ml of 16 M HNO_3 and then 10 ml of 10 M HCl. The residue was finally redissolved in 0.5 M HCl (few mls) and the solution filtered (Whatman 540, 8 μm). This solution was dried down for lead isotope analysis.

Grass samples were collected from all the plots on a regular basis, annually in the first two years but subsequently more frequently. Samples were taken using sheep shears with particular care taken to avoid the collection of soil with the grass. Immediately after cutting, a portion (approximately one half) of the grass was washed manually by immersion and gentle agitation for about 15 seconds in a 0.1% (v/v) solution of 'Teepol' (1 L) followed by a rinsing in distilled water. The grass samples, both washed and unwashed, were dried at 60°C overnight. After drying, grass samples were milled (2 mm) and portion (2–3 g) ashed for 16 hours at 450°C. The ash was dissolved in aqua regia (6 M HCl–16 M HNO_3, 3:1)(15 ml) and heated in a covered beaker on a steam bath. After removal of the cover the solution was allowed to evaporate to dryness. The residue was finally taken up in 0.5 ml HCl and the solution filtered and dried for isotope analysis.

Soil samples in the plots were sampled in two ways. Surface soil was sampled by digging an area approximately 20 cm × 20 cm to a depth of about 2 cm. Because of the limited amount of material available single surface soil samples were taken for only the first two years of the study. Auger soil samples (at least 25 individual cores bulked together) were taken to a depth of 25 cm with an even distribution throughout the plots. Ground soil samples (500 mg) were digested at 180°C in 20 M HF–16 M HNO_3 (5:1, v/v) (12 ml) in Teflon bombs for 4–5 hours. The residue was subsequently treated in the same way as plant ashes.

Determination of lead concentration

The lead concentrations in grass and soil digests were measured in portions of the solutions by inductively coupled plasma—atomic emission spectrometry (ICP-AES). The lead concentrations in rainwater samples were generally below the detection limit (0.03 $mg.l^{-1}$) of ICP-AES and for these samples the concentration was determined directly in filtered samples using graphite-furnace atomic absorption spectrometry.

Lead isotopic analysis

Lead isotope ratios were measured using a VG354 thermal ionisation mass spectrometer equipped with a 16-sample turret and a five-Faraday-cup simultaneous detection system. Samples were prepared for isotope analysis by anion-exchange chromatography on columns (10 cm long × 0.7 cm i.d., 4 ml nominal volume) packed with Bio-Rad AG 1-X8 resin (200–400 mesh, chloride form). Samples were dissolved and loaded manually in 1 M HBr (5 ml) and, after washing with 2 M HCl (10 ml), lead was eluted under gravity in 6 M HCl (10 ml). The fraction collected was evaporated to dryness under heat lamps in a fume cupboard and the residue redissolved in 0.1 M HNO_3 to give a lead concentration of about 1 $\mu g.g^{-1}$. The samples (1 μl) were loaded in duplicate on to single rhenium filaments using the silica gel technique[20] as modified by Trincherini *et al.*[21].

The lead isotope ratios were measured using a static multicollector procedure with a beam current during the measurement phase of 3×10^{-11} A. This aiming current was generally achieved at a filament current of 2.5–2.9 A and was re-established after each block of 25 ratios. The $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$ ratios were measured and averaged until no more lead was detectable on the filament thereby effectively integrating the total ion population for each isotope. The National Institute of Standards and Technology (NIST) certified reference material (CRM) 981 was used both to correct for the mass fractionation effect observed and as a check on the precision and accuracy of the procedure. Over a two year period (n = 14), analysis of NIST981 gave a measured $^{206}Pb/^{207}Pb$ ratio (uncorrected for mass fractionation) of 1.09418 ± 0.00018 (1σ) which is 0.08% higher than the certified value of 1.0933. A typical analysis of a soil sample gave duplicate measurements of the $^{206}Pb/^{207}Pb$ ratio of 1.15197 and 1.15162 with a mean of 1.1518 and a standard deviation of ±0.00025.

The four isotope ratios were measured for all samples so that any comparison did not rely on a single ratio. It is possible, for example, for two samples of lead from quite distinctly different origins to have indistinguishable $^{206}Pb/^{207}Pb$ ratios yet significantly different ratios to ^{204}Pb. The $^{206}Pb/^{207}Pb$ ratio is generally the most widely used in environmental studies and will be used in the discussion section on the basis that the other ratios confirm the conclusions reached using it.

RESULTS AND DISCUSSION

Rainwater

Rainwater lead has an isotopic composition which reflects the origin of atmospheric pollutants. Over the period of two years the $^{206}Pb/^{207}Pb$ ratios were low (Table 1), in particular at the more remote Glensaugh site, consistent with the major proportion of lead collected having its origin in petrol additives. If the ratios found in petrol in Edinburgh[17] over the same time period can be taken to be general then there is a small component of lead of other origin in rainwater collected at Glensaugh. There was a

Table 1 Lead concentrations and $^{206}Pb/^{207}Pb$ ratios in rainwater samples.

Date	*Glensaugh*		*Hartwood*	
	ng.ml^{-1}	*$^{206}Pb/^{207}Pb$*	*ng.ml^{-1}*	*$^{206}Pb/^{207}Pb$*
1/89	8.8	1.112		
2/89			8.7	1.121
2/90			10	1.115
6/90	8.7	1.121		
7/90			18	1.104
8/90	2.1	1.114	1.9	1.126
11/90	3.5	1.131	4.0	1.133
12/90	2.4	1.101	6.8	1.153
1/91	1.4	1.111	<0.3	1.133
3/91	17	1.118		
4/91			2.0	1.132
5/91			5.2	1.148

noticeable increase in the ratio measured in rainwater collected at Hartwood suggesting a larger proportion of lead from sources other than petrol. It should be noted however that there were considerable fluctuations in the measured ratios, in particular at the end of 1990, and it should be remembered that atmospheric transport of particulate matter over long distances is possible so that components of the collected lead need not be of local or even national origin. The Swedish study[14] demonstrated that large short term fluctuations in isotope ratio occur so the monthly rainwater samples represent the overall monthly trend and will smooth out day-by-day fluctuations.

Surface soils

Analyses of the surface soil samples taken at Glensaugh in 1989 and 1990 (Table 2) showed good agreement between successive year's sampling for two of the plots. There was a disrepancy for the Hillside plot but at present no explanation is available. Further data from subsequent sampling supports the 1989 result. The most noticeable difference was observed between the Roadside and other plots at Glensaugh. The $^{206}Pb/^{207}Pb$ ratio for the Roadside plot was very low and close to that observed in rainwater and to that associated with the petrol additives used in Britain at that time. Indeed it is highly unlikely that this lead could have its origin other than in passing road traffic. The ratios in the two other plots were considerably higher and showed that the two remote plots had not been dominated by the inputs of recent petrol lead. The ratios fell within the range found for Aberdeenshire galenas[22] but below the ratios associated with uncontaminated Scottish soils[3]. The relatively high lead concentrations confirmed that considerable accumulation had occurred at the surface of soils. This accumulation was comparable to that found in Scottish peat cores[23], dating of which showed that accumulation increased markedly at the start of the industrial revolution. The isotope ratios measured in the surface soils corresponded to accumulation over a long period of time and suggested that the deposition over this period can be characterized by $^{206}Pb/^{207}Pb$ ratios considerably higher than those associated with recent inputs from petrol additives.

Table 2 Lead concentrations and $^{206}Pb/^{207}Pb$ ratios in surface soils (0–2.5 cm) and auger samples (0–15 cm) from plots at Glensaugh.

Plot		*Year*	*Surface soils*		*Auger samples*	
Name	*Distance from road (m)*		*mg.kg^{-1} (air dry)*	*$^{206}Pb/^{207}Pb$*	*mg.kg^{-1} (air dry)*	*$^{206}Pb/^{207}Pb$*
Roadside	2	1989	130	1.1126		1.1483
		1990		1.1159	82	1.1413
		1991			92	1.1454
Hillside	650	1989	148	1.1536		1.1632
		1990		1.1400	104	1.1642
		1991			91	1.1650
Reseeded	900	1989	161	1.1569		1.1649
		1990		1.1556	121	1.1642
		1991			132	1.1650

It is to be noted that the lead concentrations in the surface soils distant from the road were higher than those in the roadside soil. At first sight this would appear to contradict the contention that the roadside soil is dominated by recent inputs of petrol lead for it can be expected that these would be additional to the long term inputs observed in the remote plots. There was evidence however that the soil had been disturbed by road working activity. Whereas the Hillside and Reseeded soils (sampled to a 10 cm depth) had carbon contents of 35 and 41%, respectively, the Roadside soil (sampled to the same depth) had a carbon content of only 6.4%. It is probable that a mineral soil from road diggings and uncontaminated with long term atmospheric inputs was placed on top of the organic soil previously exposed to the atmospheric inputs. The roadside soil has therefore been predominantly contaminated with recent inputs of petrol lead.

One possible explanation for the occurrence of accumulations at the surface of soils distant from the road is that of a natural movement of lead from depth by plant uptake and subsequent deposition at the surface. Such a process would be relatively constant with time and would require a very long period of time to achieve the degree of concentration required to produce the accumulations observed. If this process had indeed occurred then the data suggest that the lead accumulations consist mainly of geochemical lead with a small component of recent petrol lead. The work of Farmer and co-workers[23] on dated peat cores and loch sediments from Scotland showed clearly that significant aerial deposition occurred only from the time of the industrial revolution and that only a small proportion of the accumulations could be attributed to the deposition of recent petrol lead with a low $^{206}Pb/^{207}Pb$ ratio. Most of the deposition occurred prior to the introduction of petrol lead and was characterized by a $^{206}Pb/^{207}Pb$ ratio of 1.17. An alternative and more probable explanation for the accumulations found in soils is deposition as found in the peat samples. The ratios measured in surface soils were highly consistent with those observed for the peat and sediment samples and with the calculated changes in the isotopic character of deposited lead over time.

Lead concentrations in the Hartwood soils (Table 3) were higher than in the soils at Glensaugh. This reflected the closer proximity of the former to industrial activity. The higher $^{206}Pb/^{207}Pb$ ratio in the soil from the exposed Moor plot was evidence that lead deposition over a long time period could be associated with higher $^{206}Pb/^{207}Pb$ ratios. Such deposition would be associated with industrial activities and coal burning rather than the use of lead additives in petrol. The high concentration found in the surface soil from below the tree canopy in the Blaeberry Wood plot suggested that the tree canopy was effective in scavenging particulate matter or moisture which carried the contaminant lead. The considerably lower ratio in this sample suggested that a far higher proportion of the contaminant lead in the wooded plot had its origin in recent petrol additives than the lead in the exposed and open Moor plot.

Table 3 Lead concentrations and $^{206}Pb/^{207}Pb$ ratios in surface soils (0–2.5 cm) and auger samples (0–15 cm) from plots at Hartwood in 1991.

Plot		*Surface soils*		*Auger samples*	
Name	*Distance from road (m)*	*mg.kg^{-1} (air dry soil)*	*$^{206}Pb/^{207}Pb$*	*mg.kg^{-1} (air dry soil)*	*$^{206}Pb/^{207}Pb$*
Moor	1100	264	1.1617	78	1.1763
Blaeberry wood	700	471	1.1337	144	1.1612
Bowhouse bog	2	121	1.1612	106	1.1734

It is to be noted that the roadside soil at Hartwood (Bowhouse Bog), like the corresponding plot at Glensaugh, was the one with the lowest concentration of lead. Unlike the Glensaugh plot however the $^{206}Pb/^{207}Pb$ ratio was relatively high. This was evidence that during normal farm management of the grassland the surface soil had been removed to expose soil with lower lead concentrations and higher $^{206}Pb/^{207}Pb$ ratios.

Auger samples

The sampling approach using auger drills was designed to minimize the inhomogeneities present within the soil body and the samples collected can be considered to represent the average soil character to a depth of 25 cm throughout the plots. The measured lead isotope ratios are an average of both the surface enrichments and underlying geochemical lead and, when compared to the ratios in the surface soil samples, reflect differences in the character of the two sources. The reproducibility of sampling by this method was demonstrated by the good agreement in the lead isotope ratios measured in three consecutive years at Glensaugh (Table 2). The $^{206}Pb/^{207}Pb$ ratios in the auger samples from the Hillside and Reseeded plots were almost identical which suggested that the two soils had the same history of geochemical and added anthropogenic lead but that there had been partial redistribution during the reseeding process.

For all the plots at Glensaugh and Hartwood the $^{206}Pb/^{207}Pb$ ratios were higher in the auger samples (Tables 2 and 3) than in the surface soil samples. In all cases therefore the deeper geochemical lead had a distinctly higher ratio than the accumulated lead at the surface. This was particularly the case for the roadside soil at Glensaugh dominated at the surface by low-ratio lead and for the Blaeberry Wood soil at Hartwood which, as already noted, also had relatively-low-ratio lead at the surface. Lead accumulations at the surface of soils invariably have lower isotope ratios than lead in deeper soil and are therefore of a different and dominantly anthropogenic origin.

Grass

A comparison of lead isotope ratios measured in washed and unwashed grasses (Table 4) revealed no significant difference between the two even when all four isotope ratios were considered. Although the washing was effective in removing a substantial amount of particulate matter, in particular at the Roadside plot, this was not reflected by any change in isotopic character of the lead in or on the grass. This indicated that the lead, even that derived from atmospheric deposition, was either firmly bound to the grass surface or was incorporated within the body of the grass.

The lead isotope ratios found in grass samples at Glensaugh (Table 5) did not correspond to those found in the surface soil samples with the sole exception of the 1989 sample from the Roadside plot. In this case the very low ratio found in the grass very clearly corresponded with the ratios found in the surface soil and rainwater at that time. Although this was evidence of all three samples being dominated by the petrol lead component, it also meant that it was not possible to distinguish between the soil and atmospheric components at that plot. The following year however there was a significant increase in the $^{206}Pb/^{207}Pb$ ratio in the grass in the Roadside plot. This increase was also found in rainwater samples. Assuming that the lead from grass from the Roadisde plot was indicative of the current nature of lead derived from petrol then there was a marked increase in the $^{206}Pb/^{207}Pb$ ratio of lead used in lead additives. This confirmed the slight

Table 4 Lead isotope ratios in washed and unwashed grass samples from the Glensaugh plots.

Year	*Plot*	*Grass*	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
1989	Roadside	Unwashed	37.07	15.53	17.23	1.1095
		Washed	37.10	15.53	17.26	1.1117
	Hillside	Unwashed	37.33	15.55	17.48	1.1244
		Washed	37.35	15.55	17.50	1.1251
	Reseeded	Unwashed	37.39	15.55	17.53	1.1274
		Washed	37.32	15.54	17.53	1.1280
1990	Roadside	Unwashed	37.32	15.54	17.51	1.1272
		Washed	37.39	15.56	17.53	1.1267
	Hillside	Unwashed	37.52	15.57	17.66	1.1349
		Washed	37.54	15.59	17.68	1.1341
	Reseeded	Unwashed	37.54	15.56	17.69	1.1366
		Washed	37.60	15.58	17.73	1.1385

Table 5 $^{206}Pb/^{207}Pb$ ratios in unwashed grass samples from Glensaugh plots.

Year	*Plot*	$^{206}Pb/^{207}Pb$
1989	Roadside	1.1095
	Hillside	1.1244
	Reseeded	1.1274
1990	Roadside	1.1272
	Hillside	1.1349
	Reseeded	1.1366

increase (1.062–1.083) in the petrol lead $^{206}Pb/^{207}Pb$ ratio observed by Sugden *et al.*[17] from 1989 to 1991 with one measured ratio of 1.142.

The isotope ratios found in grass in the other two plots at Glensaugh were significantly higher than that in the roadside grass but the ratios also increased significantly from 1989 to 1990. This suggested that whereas there was one dominant component at the roadside site (direct deposition from car emissions) this was not the case distant from the road. Petrol additives were still an important source as reflected by the observed increase from 1989 to 1990 but there was another significant component. One can only speculate at the source of this other component at this stage but industrial emissions and coal burning are probable sources. In all cases the lead is probably deposited following long range atmospheric transport.

Lead isotope ratios in grass samples collected at the Hartwood plots in 1991 (Table 6) reflected those found in the grass samples from Glensaugh during 1989 and 1990. The low ratio found in the roadside grass at the Bowhouse Bog plot confirmed that the origin of the lead was in petrol and that the high ratio found in the surface soil did not represent current inputs. It is perhaps surprising that the isotope ratio found at Hartwood during 1991 was still low whereas the low ratio found at Glensaugh in 1989 had already been replaced by a higher ratio by 1990. This further emphasises the need to consider each situation in isolation. The isotope ratios in the two plots at Hartwood distant from the road (Moor and Blaeberry Wood) were considerably higher than both the ratio at the roadside site and the ratios at the corresponding Glensaugh plots. This confirmed the existence of a second component away from road traffic which was in higher proportion at Hartwood closer to sources of industrial emissions. The $^{206}Pb/^{207}Pb$ ratio associated with this second component must be > 1.14.

The surface soil at the Blaeberry Wood plot at Hartwood lies beneath a tree canopy and it has already been noted that the lead concentration (471 mg.kg^{-1}) is high and that the $^{206}Pb/^{207}Pb$ ratio is low (1.1337). Grass and fallen leaves collected from the plot also have low ratios but that for the leaves (1.1372) is noticeably lower than that for the grass (1.1414). A possible explanation for this difference is that the lead in the grass also has a small component derived from the soil either by direct uptake or by surface contamination through air or insect movement. If this were the case then, assuming that the leaves would have a smaller and insignificant component from the soil, contamination or uptake could not be from the surface soil which has a lower $^{206}Pb/^{207}Pb$ ratio than either the leaves or grass. The ratio for the leaves is strikingly close not only to the ratio in surface soil but also to the ratios (1.1349 and 1.1366) found in the grass samples at Glensaugh in 1990. It is not possible to satisfactorily explain the difference in the ratios in grass and leaves at the same plot. It could be that the leaves represent total aerial deposition whereas the grass samples have another additional component, perhaps soil from greater depth. Alternatively the two sample different proportions of the components of deposition, for example dry particulate deposition and occult deposition.

The $^{206}Pb/^{207}Pb$ ratios of 1.1372 and 1.1414 found in the leaves and grass are close to the ratios (1.135–1.137) measured in sediments from Swansea Bay and soil from South Wales and associated with South Wales coal and other industries[9], to the ratio (1.141) found in the vicinity of French industrial plants[10], to the mean ratio (1.142) found in Swedish aerosols and associated with air movement from Western Europe[14], to the ratios (1.140 and 1.141) associated with air masses in the North Sea originating from Continental Europe[13] and to the ratio (1.143) found in surface peat in a remote area of Scotland[19]. It would appear that a $^{206}Pb/^{207}Pb$ ratio of about 1.140 is strongly associated with atmospheric inputs of mainly industrial origin. The value of 1.140 was also adopted as representative of atmospheric lead in Eurasia and Canada by Rosman *et al.*[24].

Table 6 $^{206}Pb/^{207}Pb$ ratios in unwashed grass samples from Hartwood plots in 1991.

Plot	*Distance from road (m)*	*$^{206}Pb/^{207}Pb$*
Moor	1100	1.1494
Blaeberry wood	700	1.1414
Bowhouse bog	2	1.1180

CONCLUSIONS

The use of stable isotope composition gives evidence for the nature and origin of lead accumulations found at the surface of soils even in remote areas of upland Scotland. This study has characterised the lead present in accumulations in surface soils, which represent past atmospheric deposition, and in grass and rainwater, which represent current inputs from the atmosphere. It has been shown that grass and rainwater samples are good indicators of the current inputs from the atmosphere averaged out over short periods of time. The main input beside a road was from passing traffic but away from the road there were at least two main components. One was associated with petrol additives whereas the others were of a different origin, probably industrial. The nature of this deposition varied on a short timescale and it is therefore critical in the use of isotopic composition to characterise each individual situation both in terms of time and geographical location.

The lead isotope composition in undisturbed surface soil represents an accumulated record of aerial deposition over a long timescale. This study has shown that the lead in surface soils distant from the road has an isotopic character different from current aerial inputs yet the concentrations are as high as those from beside roads. It can be concluded that the lead accumulations in surface soils distant from the road are not as a result of the low ratio lead used in the recent past in petrol additives. They are of considerable age and were formed when the $^{206}Pb/^{207}Pb$ ratio of atmospheric deposition was considerably higher, either from industrial sources which still have a higher $^{206}Pb/^{207}Pb$ ratio than petrol additives or from petrol additives with higher $^{206}Pb/^{207}Pb$ ratios than currently found. Historical inputs dominate the accumulations in soils distant from road traffic and this evidence is consistent with the conclusions of other studies[23] that the accumulation of lead in the environment has been a continuous process from the beginning of, if not before, the industrial era. The total lack of environmental controls and the widespread use of fossil fuels resulted in widespread pollution of the environment in even the remotest parts and this probably still dominates the accumulations found to this day.

This study has found the washing of grass samples to be ineffective. It could be concluded that the washing process itself was not sufficiently efficient but in fact it did remove a considerable amount of particulate matter. It can be concluded that no lead is taken up from the soil by the plant and that the lead in the grass has its origin almost solely in the atmospheric deposition. If there is a contribution from the surface soil through root uptake it is very small but it is not possible at this stage to discount a soil component because of the heterogeneous nature of the soil and the possibility that grass roots sample soil from greater depth. The lead isotope analysis of grass and leaves from the same plot demonstrated that there are significant differences between them. At this stage it is not possible to explain this but an explanation would be that the grass and leaves sample different components of the deposited lead.

The use of lead isotopic composition in environmental studies is of considerable value in characterising inputs into the environment and their relationship to the accumulations already present, in particular in the soil. The method also has considerable potential in assessing the fate of the heavy metals and for studying the processes that take place within the soil. It is important to understand the changes that could occur in the mobility and bioavailability of metals as soils or environmental conditions change. The use of stable isotopic composition gives direct access to this information. Lead isotope ratios found in environmental samples in Britain fall within a wide range and consequently the analytical requirements are not very demanding. The very high precision demonstrated in this study allows small but significant differences in ratios to be measured, however.

This is of importance when the ratios fall within a narrow range, for example in the case of the grass and leaves from one site probably involving more than one component of similar isotopic character. To differentiate between these and to make progress in further studies on the chemical form and association of the different components it is essential to have high performance analysis.

References

1. C. C. Patterson, *Conn. Med.*, **35**, 347–352 (1971).
2. B. E. Davies, D. Conway and S. Holt, *J. Agric. Sci. (Camb.)*, **93**, 749–752 (1979).
3. J. R. Bacon, M. L. Berrow and C. A. Shand, *Intern. J. Environ. Anal. Chem.*, **46**, 71–76 (1992).
4. A. Nier, *J. Am. Chem. Soc.*, **60**, 1571–1576 (1938).
5. T. J. Chow and M. Johnson, *Science*, **147**, 502–503 (1965).
6. M. B. Rabinowitz and G. W. Wetherill, *Environ. Sci. Technol.*, **6**, 705–709 (1972).
7. T. J. Chow, C. B. Snyder and J. L. Earl, in: Isotope Ratios as Pollutant Source and Behaviour Indicators (IAEA, Vienna, 1975) pp. 95–107.
8. B. L. Gulson, K. G. Tiller, K. J. Mizon and R. H. Merry, *Environ. Sci. Technol.*, **15**, 691–696 (1981).
9. E. I. Hamilton and R. J. Clifton, *Estuarine and Coastal Marine Sci.*, **8**, 271–278 (1979).
10. F. Elbaz-Poulichet, P. Holliger, J. M. Martin and D. Petit, *Sci. Total Environ.*, **54**, 61–76 (1986).
11. Y. Hirao, H. Mabuchi, E. Fukuda, H. Tanaka, T. Imamura, H. Todoroki, K. Kimura and E. Matsumato, *Geochem. J.*, **20**, 1–15 (1986).
12. H. Maring, D. M. Settle, P. Buat-Menard, F. Dulac and C. C. Patterson, *Nature (London)*, **330**, 154–156 (1987).
13. M. Kersten, U. Foerstner, P. Krause, M. Kriews, W. Dannecker, C. -D. Garbe-Schoenberg, M. Hoeck, U. Terzenbach and H. Grassl, in: *Trace Metals in the Environment. Vol. 2* (J. -P. Vernet, ed. Elsevier, Amsterdam, 1992) pp. 311–325.
14. J. F. Hopper, H. B. Ross, W. T. Sturges and L. A. Barrie, *Tellus*, **43B**, 45–60 (1991).
15. S. Fachetti and F. Geiss. *Commission of the European Communities*, Report No. EUR 8352 EN (1984).
16. M. Keinonen, *Sci. Total Environ.*, **113**, 251–268 (1992).
17. C. L. Sugden, J. G. Farmer and A. B. MacKenzie, *Environ. Geochem. Health*, **15**, 59–65 (1993).
18. H. T. Delves, *Chem. Brit.*, **24**, 1009–1012 (1988).
19. C. L. Sugden, J. G. Farmer and A. B. MacKenzie, in: *Proceedings of the Eighth International Conference on Heavy Metals in the Environment*, Vol.1 (CEP, Edinburgh, 1991) pp. 90–93.
20. P. A. Akishin, O. T. Nikitin and G. N. Panchenkov, *Geokhimiya*, **5**, 425–429 (1957).
21. P. R. Trincherini, S. Contini and L. Perucchini, *Determination by Mass Spectrometry of the Isotopic Ratio Pb 206/Pb207 in Metal (SRM) and in Blood Samples*, Application Report No. 49, Finnigan MAT, Bremen, Germany, 1981.
22. S. Moorbath, *Phil. Trans. Roy. Soc. Lond. A*, **254**, 295–360 (1962).
23. J. G. Farmer, A. B. MacKenzie, C. L. Sugden, C. L. Bryant, L. J. Eades, A. E. Bailey-Watts and A. Kirika, in: *Proceedings of the Ninth International Conference on Heavy Metals in the Environment*, Vol. 2 (CEP, Edinburgh, 1993) pp. 211–214.
24. K. J. R. Rosman, W. Chisolm, C. F. Boutron, J. P. Candelone and U. Gorlach, *Nature (London)*, **362**, 333–335 (1993).